Equilibrium studies of gas phase ion–molecule reactions. Ion cyclotron resonance results for the reaction $CO_2H^+ + CH_4 \rightleftharpoons CH_5^+ + CO_2$

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The recent application of mass spectrometric techniques to the determination of equilibria in gas phase ion–molecule reactions has provided an abundance of thermochemical data relating to the intrinsic (gas phase) stability[1–11] and solvation energetics[4,12,13] of ionic species. Ion cyclotron resonance (ICR),[1–4] flowing afterglow (FA),[5,6] high pressure mass spectroscopy (HPMS),[7–10] and trapping of ions in the space charge of an electron beam of standard mass spectrometers (TIMS)[11] have all been applied in the investigation of reversible ion–molecule reactions under conditions where equilibrium may be attained. Not surprisingly, a healthy skepticism has developed regarding the validity of the assumption that equilibrium is truly established in these experiments, which are performed under vastly different conditions of gas density, ion residence times, and applied electric fields. A comparison of results using different techniques is particularly valuable, and for this reason we wish to report ICR results for the reversible proton transfer Reaction (1). The disparity of results

$$CO_2H^+ + CH_4 \underset{k_r}{\overset{k_f}{\rightleftharpoons}} CH_5^+ + CO_2 \qquad (1)$$

obtained with other techniques which have been applied to study Reaction (1) are evident in the data summarized in Table I.

The investigation of Reaction (1) utilizing ICR techniques is straightforward.[1–3,14,15] In a mixture of CO_2 and CH_4, the equilibrium is rapidly established, permitting determination of K_{eq}. After equilibrium is established, delayed ion ejection techniques yield separately the forward and reverse rate constants.[3] For example, if CH_5^+ is ejected continuously, CO_2H^+ will disappear with the rate constant k_f. Similarly, ejection of CO_2H^+ leads to the disappearance of CH_5^+ with rate constant k_r. The results of such measurements, performed at ambient temperatures (~296 °K) with varying ratios of CO_2 and CH_4 at total pressures around 7×10^{-6} torr, are included in Table I for comparison to previous measurements.

The ICR results for Reaction (1) are seen to be in excellent agreement with the flowing afterglow studies, including the equilibrium constant and the separately determined forward and reverse rate constants. In both cases, the ratio k_f/k_r is in agreement with the independently determined value for K_{eq} to within the uncertainty imposed by the error limits for k_r. The agreement of the results obtained by the FA and ICR techniques is particularly significant in view of the fact that gas densities are six orders of magnitude lower in the ICR experiments, and a buffer gas is apparently not required for equilibrium to be established. The forward reaction rate determined in the space charge trapping experiments of Harrison and coworkers is in good agreement with both the FA and ICR results. These authors discuss at some length possible reasons for the low value of the apparent equilibrium constant obtained in their work. In the TIMS experiments the space charge of an electron beam creates a potential well in which the ions are confined until an extraction field is applied to sample ion concentrations.[11] This is not unlike the trapped ion ICR experiments in which electric fields of comparable magnitude are applied to confine ion motion in the direction of the primary magnetic field.[14,15] Assuming pressure measurements or determination of mixture compositions is not a problem, it appears that the space charge trapping experiments must leave the ions with an epithermal energy distribution. Proton transfer reactions such as (1) provide an efficient means for relaxing internal excitation in ions which may be retained when they are initially formed in exothermic processes. In ICR experiments an epithermal distribution of ion energies is collisionally relaxed by several collisions with neutral gas molecules. In the TIMS experiments, however, electron–ion interactions may lead to a continuing source of excitation which maintains the epithermal energy distribution of the ions. This possibility might be investigated by studying K as a function of electron beam current. While relaxation of the initial epithermal energy distribution is rapid compared to source residence times

TABLE I. Rate and equilibrium constants for the reaction $CO_2H^+ + CH_4 \rightleftharpoons CH_5^+ + CO_2$ as determined by several mass spectrometric techniques.

Method	T, °K	k_f[a]	k_r[a]	K_T	$K_{298.15}$[b]
FA[c]	296	7.8±0.2	0.33±0.1	24.8±1	24.4±1
HPMS[d]	340	1.3	•••	7.5	9.0
TIMS[e]	373	6.1±0.5	•••	4.0	4.7
ICR[f]	296	7.9±1	0.36±0.1	24.7±1	24.3±1

[a] 10^{-10} cm^3 molecule^{-1} · sec^{-1}.
[b] Calculated from K using $\Delta S = 1.4$ e.u. (Ref. 5).
[c] Reference 5, error limits represent the authors' estimates of the precision.
[d] Reference 7.
[e] Reference 11.
[f] Present work. Values given are an average over at least three independent determinations for a range of pressure ratios varying by at least a factor of 1.7. Error limits represent the authors' estimates of the accuracy of the measurements, the principal source of error being uncertainties in pressure determinations. In all cases the precision, as determined by the range of the experimental values, was substantially better than this error estimate.

for FA, ICR, and TIMS, the residence times of ions and gas densities employed in the source used for the HPMS experiment were not sufficient for relaxation of the ion energy distribution and hence for equilibrium to be established.[11,16]

Further comparisons of the various techniques for determination of equilibria in gas phase ion–molecule reactions will prove useful. It would be of particular interest to resolve the difficulties which appear to invalidate the assumption that equilibrium is established in the TIMS experiments since most standard mass spectrometers can be equipped to perform such experiments at pressures below those normally used to investigate ion–molecule reactions.[17]

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Reaction of C_2H^+ with H_2 *

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Using the crossed-beam machine EVA,[1] we measured product angular and velocity distributions for

$$C_2H^+ + D_2 \rightarrow C_2D^+ + HD\,, \quad (1)$$

$$C_2H^+ + D_2 \rightarrow C_2HD^+ + D\,, \quad (2)$$

$$C_2H^+ + D_2 \rightarrow C_2D_2^+ + H, \quad (3)$$

$$C_2D^+ + H_2 \rightarrow C_2DH^+ + H\,, \quad (4)$$

over a range of relative (c.m.) energies of 0.3–6 eV. Contour maps of the product velocities show complicated behavior for (2)–(4). At the lower energies the ion products are all well forward of the center of mass (C_2H^+ beam direction) and show negligible intensity behind the center of mass. At intermediate energies, as shown in Fig. 1, the products are near the center of mass. At higher energies, products near the center of mass have enough energy to dissociate, and the peaks shift forward again. For $0.3 < E_r < 4$ eV the cross section for (3) is ~15% of that for (2).

Q, the average translational exoergicity, spans a wide range for (2), from $Q = +0.6$ eV at $E_r = 0.2$ eV to $Q = -3.5$ eV at $E_r = 5$ eV. If a single mechanism is responsible for (2)–(4), only two states can support such a wide range of internal energies, the acetylene ion HCCH$^+$ ($\Delta H = -1.3$ eV)[2] and the vinyledene carbene cation CCH_2^+ ($\Delta H = +0.3$ eV).[3] To produce the carbene cation, the Q values at low energy require the conversion of over 1 eV of internal energy in C_2H^+ into translational energy of the products. This is unlikely, and thus the acetylene ion is the probable product.

As shown in Fig. 1, at intermediate energies the product of (2) is further from the center of mass than the product of (3). Yet the product of (4) which is the isotopic mirror image of (2) is close to the center of mass, implying that the final velocity is governed by the product masses rather than by the reactant configuration. This may be the result of a greater centrifugal barrier when H is the leaving atom. As a very crude model we

